stop solution (a solution that stops the reaction from proceeding) can be added to each drop at different locations in the chamber, resulting in different times of reaction. Then the drops can be assayed as the tape leaves the chamber, and kinetic rate constants can be obtained from the data.

[0088] The fourth method is to add a reaction "start" solution to the drops at different places in the chamber, such that the drops are reacting at different times and hence duration before they are analyzed.

[0089] Analysis

[0090] The samples need not be transferred to conventional types of chemical vials or multi-well plates for most types of analysis. Many types of chemical assays can be performed directly on the chemical reaction products as they moved via the moving surface. Non-destructive spectroscopic methods such as fluorescence, phosphorescence, fluorescence polarization, Raman, nuclear magnetic resonance (NMR) and absorption spectroscopy can be performed on the samples as they are moved to appropriate positions for the assays to be performed. In various embodiments of the invention, the droplet is hung from the moving surface while being analyzed, the droplet adhering to the moving surface through, at least in part, surface tension. In a preferred embodiment, a spectrometric analysis technique, such as mass spectrometry, can be performed by removing aliquots of the sample at specific points via the moving surface. The ability to translocate the sample using the moving surface allows for multiple types of spectroscopic and/or spectrometric assays to be performed on each sample in a sequential manner. Multiple designs for delivering a sample from a moving surface to an analyzer, such as a mass spectrometer, are possible. These may include, but are not limited to, the following approaches.

[0091] Standard Fluidic Systems

[0092] **FIG. 9** is a schematic diagram of a valve assembly **107** that removes the sample **102** to be interrogated from the moving surface **101** by aspiration, in accordance with one embodiment of the invention. The sample **102** to be interrogated is removed from moving surface **101** by aspirating it off of the moving surface **101** through a length of narrow-bore capillary tubing **104**. The sample is then directed to a valve **106**. The actuation of this valve **106** will deliver the sample to an analyzer **105**, such as a mass spectrometer. Initially the sample is aspirated into the valve **112** as shown in **FIG. 10**. Enough of the sample to fill a length of tubing **112** with a defined volume is aspirated. Upon actuation of the valve **122**, this metered amount of the sample is directed through a narrow bore capillary **121** to the analyzer **123**, such as a mass spectrometer, as shown in **FIG. 11**. The sample may be presented to the analyzer **123** using a variety of standard systems, including atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI).

[0093] Additional sample preparation steps may be performed while the droplet is in the valve. Prior to delivery to the analyzer the sample can be presented to a matrix of one or more types of immobilized or insoluble resins, beads, polymers, or particles with or without surface coatings for the removal of salts or other contaminants. The removal of contaminants with such a system can occur by the selective adsorption of the undesirable contaminants with the analyte of interest not being adsorbed and presented to the mass spectrometer. In an alternative embodiment of the invention, the sample is selectively adsorbed to the matrix under one set of conditions but is desorbed from the matrix under another set of conditions. The cleanup procedure could take place before, within, or after the valve assembly.

[0094] Piezo-electric Dispensing Units

[0095] **FIG. 12** is a schematic diagram of a piezo-electric unit assembly **135** that removes the sample **133** to be interrogated from the moving surface **131** by aspiration, in accordance with one embodiment of the invention. If desired, the sample **133** to be aspirated can be desalted or purified of contaminants prior to aspiration into a piezo-electric unit **132**, which may be positioned by a position arm **134**. Sample **133** to be interrogated is then dispensed from piezo-electric unit **132** and analyzed, for example, by a mass spectrometer. The piezo-electric system **146** could dispense the sample **143** in a stream of very small droplets **141**, as shown in **FIG. 13**, similar to atomization that takes place in standard electrospray ionization mass spectrometry (ESI-MS). By adjusting the geometry of the stream of droplets **141**, the MS inlet **145** temperature, and the flow rate and geometry of the sheath gas enough solvent can be evaporated from the micro-droplets **141** for direct analysis of the resulting ions by mass spectrometry.

[0096] In an alternative embodiment of the invention, a piezo-electric unit **151** can deliver the sample in the form of a stream of micro-droplets **154** to a surface **152** proximal to the inlet orifice **153** of the mass spectrometer, as shown in the piezo-electric system **155** depicted in **FIG. 14**. The resulting atomization that takes place because of the splashing of a droplet after a high-speed collision with a surface is similar to that in ESI-MS. The surface to which sample stream **154** is directed could be coated with a variety of hydrophobic or hydrophilic coatings, its position and geometry could be optimized and an electric charge can be applied to the surface and the surface can be heated to assist in the optimal sample ionization and atomization for delivery to the mass spectrometer. The geometry of sample stream **154**, inlet **153** temperature, and the flow rate and geometry of the sheath gas can also be optimized. In another embodiment, a piezo-electric unit **161** can deliver a sample in the form of a stream of micro-droplets **164** at the point of a sharp pin or needle **162** that is in proximity to the inlet orifice **1653** of the mass spectrometer, as shown in **FIG. 15**. Alternatively, the piezo-electric unit **171** can deliver a sample in the form of a stream of micro-droplets **164** to a fine mesh in proximity to the inlet orifice **1653** of the mass spectrometer, as shown in **FIG. 16**. The micro-droplets will further atomize upon hitting this surface and further disperse into an atomizing spray, similar to that in most atmospheric pressure ionization schemes currently used. The geometry and shape of the needle or pin with respect to the MS inlet orifice or the sample stream can be optimized to provide the largest amount of atomization. The surface of the pin or needle can be coated with a hydrophobic or hydrophilic surface and a voltage can be applied to the pin to optimize the atomization process. Additionally, a gas such as methane or ammonia can be introduced to the atomization chamber to perform a chemical ionization.

[0097] In another embodiment of the invention, the droplet stream **185** from the piezo-electric unit **186** can be